

APPENDIX A

MO-5664
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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICANTS: REINHOLD KLIPPER ET AL
SERIAL NO.: 10/687,780
FILED: OCTOBER 17, 2003
FOR: PROCESS FOR PREPARING MONODISPERSE ION EXCHANGERS
HAVING CHELATING FUNCTIONAL GROUPS AND THE USE
THEREOF
GROUP NO: 1713
EXAMINER: T. ZALUKAEVA

DECLARATION UNDER 37 CFR 1.132

I, Reinhold Klipper of Gellenkircherstr. 29, 50933 Cologne, Germany, declare as follows:

1. I studied chemistry at the University of Cologne and obtained a doctorate in chemistry in 1978. Since 1981 I have been employed by Bayer AG in Leverkusen, Germany, as a research chemist for development of new ion exchangers. With the spin-off of Bayer's Chemicals division in 2005 I am now employed at Lanxess Deutschland GmbH as a research chemist in the Business Unit ION-EXCHANGERS.
2. I am an inventor of and familiar with the subject matter of the above-identified United States patent application.
3. I performed or supervised the following experiments:

New Example 2 for the manufacturing of a macroporous, monodisperse chelating ion exchanger with aminomethyl phosphonic acid groups according to the present invention (by the so called phthalimide process)

- 2a) Preparation of the monodisperse macroporous bead polymer based on styrene, divinylbenzene, and ethylstyrene (the same procedure as already described for Example 1 on page 12 of the specification)
- 3000 g of deionized water were placed in a 10 liter glass reactor, and a solution made from 10 g of gelatin, 16 g of disodium hydrogen phosphate dodecahydrate, and 0.73 g of resorcinol in 320 g of deionized water was added and thoroughly mixed. The temperature of the mixture was controlled to 25 °C. Then, with stirring, a mixture made from 3200 g of microencapsulated monomer droplets with a narrow particle size distribution and made from 3.6% by weight of divinylbenzene and 0.9% by weight of ethylstyrene (used in the

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form of a commercially available isomer mixture of divinylbenzene and ethylstyrene in 80% of divinylbenzene), 0.5% by weight of dibenzoyl peroxide, 58.2% by weight of styrene, and 38.8% by weight of isododecane (industrial isomer mixture with a high proportion of pentamethylheptane), wherein the microcapsules were composed of a formaldehyde-hardened complex coacervate made from gelatin and from a copolymer of acrylamide and acrylic acid, was introduced and 3200 g of aqueous phase with a pH of 12 was added. The average particle size of the monomer droplets was 460 µm.

The mix was polymerized to completion, with stirring, by increasing the temperature according to a temperature program starting at 25°C and finishing at 95°C. The mix was cooled, washed using a 32 µm screen, and then dried in vacuo at 80°C. This gave 1893 g of a spherical polymer with an average particle size of 440 µm, narrow particle size distribution, and a smooth surface.

The polymer had a chalky appearance from above and had a bulk density of about 370 g/l.

- 2b) **Preparation of the amidomethylated bead polymer**
 1507.1 g of dichloroethane, 305 g of phthalimide, and 218.3 g of 29.2% strength by weight formalin were placed in a vessel at room temperature. The pH of the suspension was adjusted to from 5.5 to 6 using aqueous sodium hydroxide. The water was then removed by distillation. 22.4 g of sulfuric acid were then metered in and the resultant water was removed by distillation. The mix was cooled. 817 g of 65% strength oleum were metered in at 30°C, followed by 220.2 g of monodisperse bead polymer prepared according to process step 2a). The suspension was heated to 70°C and stirred for a further 6 hours at this temperature. The reaction liquid was drawn off, deionized water was metered in, and residual dichloroethane was removed by distillation.

Yield of amidomethylated bead polymer: 1100 ml

Composition by elemental analysis:

carbon: 77.3% by weight;
 hydrogen: 5.1% by weight;
 nitrogen: 5.2% by weight;

Remainder oxygen.

- 2c) **Preparation of the aminomethylated bead polymer**
 974 ml of 20% strength by weight aqueous sodium hydroxide were metered at room temperature into 1070 ml of amidomethylated bead polymer. The suspension was heated to 180°C and stirred for 6 hours at this temperature.

The resultant bead polymer was washed with deionized water.

Yield of aminomethylated bead polymer: 875 ml

Composition by elemental analysis:

carbon: 81.4% by weight;
 hydrogen: 8.2% by weight;
 nitrogen: 9.5% by weight;
 oxygen: 1.9% by weight.

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From the composition of the aminomethylated bead polymer by elemental analysis, it could be calculated that on statistical average per aromatic ring – stemming from the styrene and divinylbenzene units – 1.01 hydrogen atoms were substituted by aminomethyl groups.

2d) Preparation of the ion exchanger having chelating aminomethyl phosphonic acid groups

400 ml of aminomethylated bead polymer from Example 2c) were metered into 208 ml of deionized water. Without cooling 215.6 g of dimethyl phosphite were metered into this suspension within 16 minutes. The mixture was stirred for 30 minutes.

Then 668 g of sulfuric acid monohydrate were added dropwise for 4 hours while the temperature should not reach more than 90°C. After completion of addition of the sulfuric acid monohydrate the temperature was raised to 100°C and 304.3 g of 29.8% strength by weight formalin were added. The resulting suspension was allowed to reflux for additionally 6 hours under stirring.

The suspension was then cooled, the ion exchanger filtered off and placed into a glass column. From the top of the column 4% strength by weight aqueous sodium hydroxide was metered until the ion exchanger was recharged from the H(protionic) form into the Na(sodium) form. Finally the ion exchanger was classified to remove soluble and solid particles.

Yield of ion exchanger having aminomethyl phosphonic acid chelating groups:

H-form: 610 ml

Na-form: 915 ml

Total capacity of the resin: 3,348 mol/l

Composition by elemental analysis:

nitrogen: 4.1% by weight

phosphorous: 13.0% by weight

Molar ratio phosphorous to nitrogen: 1.43 : 1

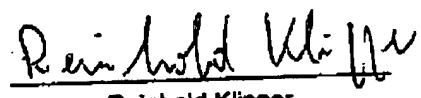
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4. The experiment shows that the total capacity of a presently claimed monodisperse resin with aminomethyl phosphonic acid chelating groups in the sodium form with 3,348 mol/l is much higher than the total capacity of a heterodisperse resin with aminomethyl phosphonic acid groups in the sodium form according to US 5,804,608 Example 2 in Table 1, which is only 1,5 meq/ml.
5. The undersigned declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United

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States Code and that such willful false statements may jeopardize the validity of the application or
any patent issuing therefrom.

Signed at Leverkusen, Germany, this 22th day of August 2005.


Reinhold Klipper

APPENDIX B

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 EXAMINER: T. ZALUKAEVA

DECLARATION UNDER 37 CFR 1.132

I, Bruno Hees of Zum Stadion 55, 40764 Langenfeld, Germany, declare as follows:

1. I studied ceramic chemistry and applications at the University of Applied Sciences (UAS), Höhr-Grenzhausen, department of UAS, Koblenz, Germany, and obtained a graduate engineer in ceramics in 1967. Since 1967 I have been employed by Bayer AG in Leverkusen, Germany, and since 1999 as a senior engineer for development of applications by new ion exchangers. With the spin-off of Bayer's Chemicals division in 2005 I am now employed at Lanxess Deutschland GmbH as a senior engineer in the Business Unit ION-EXCHANGERS.
2. I am an inventor of and familiar with the subject matter of the above-identified United States patent application.
3. I performed or supervised the following experiments:
 Performance of laboratory trials for Cu adsorption (noble metal) on ion exchange resins with functional groups of iminodiacetic acid (IDA)

Laboratory trials were carried out using a small glass column with the dimensions internal diameter = 22 mm and column height = approx. 400 mm. This column contained a porous glass frit carrier on the bottom of the column.
 The synthetic feed solution was prepared in a plastic tank with 200 litres of volume using demineralised water
 + 18 mg Cu²⁺/L, using salt of Cu(II)-sulfate,
 + 620 mg H₂O₂/L as an additional component, using commercial grade of peroxide solution (30%),
 subsequently with pH adjustment to pH 4 to 5, if necessary, using sulfuric acid.

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This solution was steadily pumped through the column using a peristaltic pump. The flow direction was upwards. The pump was adjusted to reach a specific flow rate of 40 bedvolumes per hour (bedvolume=BV=installed volume of resin in service form). The effluent from the top of the column was sampled time by time and these effluent samples were analyzed for Cu content by AAS.

Samples of a heterodisperse resin according to the prior art such as US 5,804,606 and a monodispersed resin according to the present invention were available in their Na-form.

For the comparison test both samples had to be transferred from the Na-form into their H-form.

Therefore 100 ml of the resin samples were exactly measured in their delivery form, then regenerated by 2 BV of H₂SO₄ 10% and rinsed by 5 BV demineralised water to obtain their H-form.

Due to the shrinking the resulting resin volumes were 74 ml (heterodispersed resin) and 78 ml (monodispersed resin) resp.

The trials run successively in order to adjust the peristaltic pump and to secure the same specific flow rate of 40 BV/h for the different quantities of resin samples in H-form. The throughput was calculated in BV and the chart shows the residual Cu content in the effluent samples at several BV throughput. After full breakthrough of Cu on the heterodisperse resin (according to the prior art) has been attained the corresponding throughput was used also as maximum for the monodisperse resin.

4. The experiment shows that presently claimed monodisperse resins with iminodiacetic acid chelating groups in the sodium form having higher total capacities than the heterodisperse resins with iminodiacetic acid chelating groups in the sodium form according to US 5,804,606 show a significant higher operating capacity and no increase of Cu leakage and therefore no breakthrough through the column (see the attached chart)
5. The undersigned declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing therefrom.

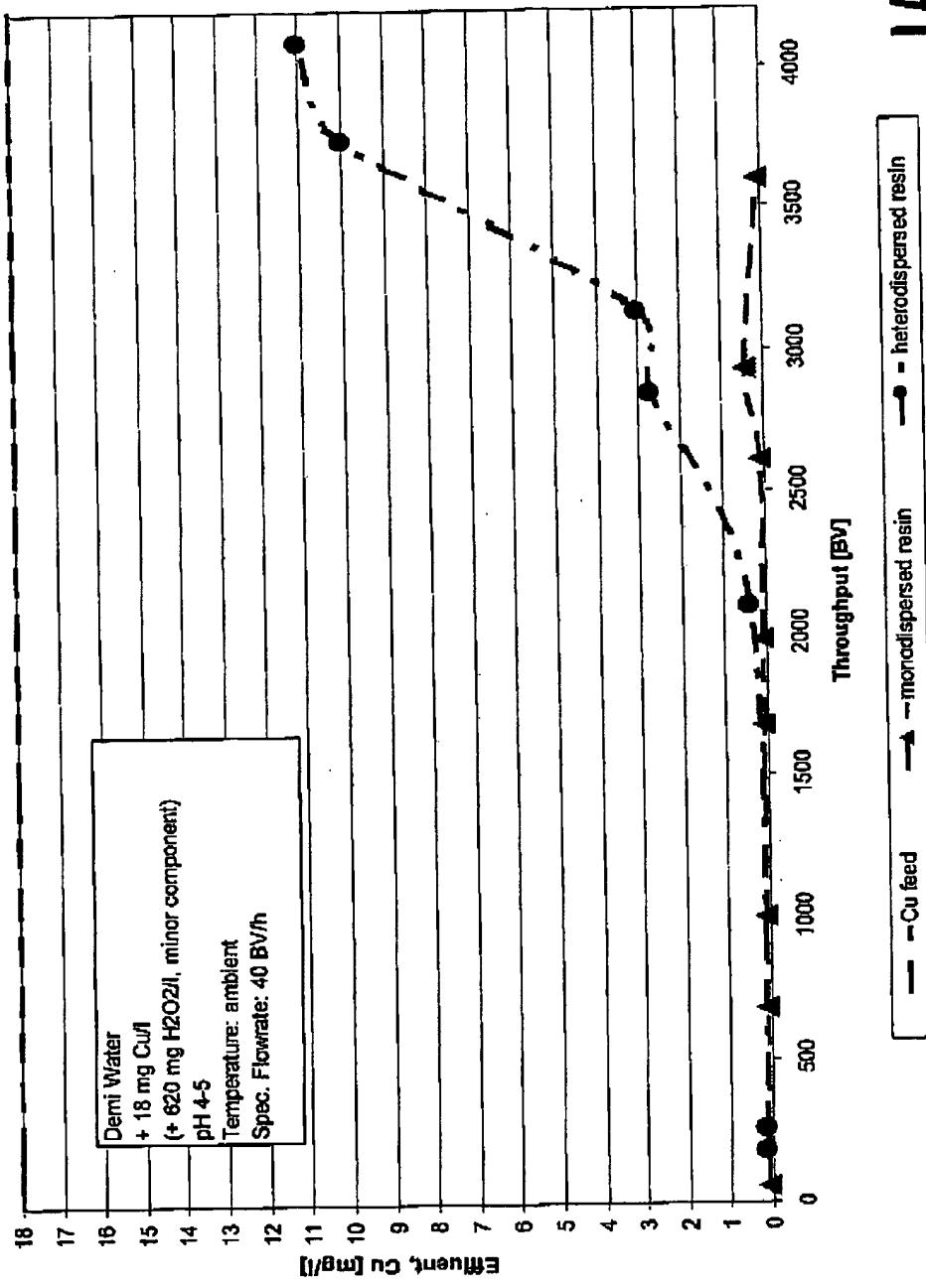
Signed at Leverkusen, Germany, this 31st day of August 2005.

Bruno Hees

Bruno Hees



Cu Load on IDA Resins In Fluid Bed
Service Form = H-Form



Comparison Cu on IDA resin HD vs. HD / Bruno Hees
 2005-09-25

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